EFFECT OF ZINC BORATE AND FILLER LOADING ON THE PROPERTIES OF POST BIODEGRADATION MERANTI WOOD FLOUR FILLED RECYCLED HIGH DENSITY POLYETHYLENE (rHDPE) COMPOSITE

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by

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
BAE	Boric acid equivalent
DP	Degree of polymerization
DSC	Differential Scanning Calorimetry
DTGA	Derivative Thermogravimetric Analysis
FRIM	Forest Research Institute of Malaysia
FSP	Fiber Saturation Point
FTIR	Fourier Transform Infra Red
HDPE	High density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MAPE	Maleic anhydride polyethylene
MFI	Melt Flow Index
MSW	Municipal solid waste
PBS	***Poly (butylene succinate***)
PE	Polyethylene
PF	Phenol formaldehyde
PLA	Poly (lactic acid)
PP	Polypropylene
PS	Polystyrene
PV	Pressure velocity
PVC	Polyvinyl Chloride
rHDPE	Recycled High density polyethylene
FESEM	Field Emission Scanning Electron Microscopy
SIRIM	Standard Research Institute Malaysia
TAPPI	Technical Association of Pulp and Paper Industry
TGA	Thermogravimetric Analysis
ULDPE	Ultra low density polyethylene
UHMWPE	Ultrahigh molecular weight polyethylene
UF	Urea formaldehyde

UV	Ultraviolet
WF	Wood flour
WPCs	Wood Plastic Composites
XPS	X-ray photoelectron spectroscopy
ZB	Zinc Borate

LIST OF SYMBOLS

%	Percentage
^{o}C	Degree Celsius
ΔH_f	Heat of fusion of the polymer
ΔH_{f100}	Heat of fusion for a 100% crystalline polymer
rpm	Rotation per minute
T_m	Melting point
T_c	Crystallization temperature
wt.%	Weight percentage
χ_c	Degree of crystallinity
α	Alpha
β	Beta
γ	Gamma
ρ	Density
<	Less than

KESAN ZINK BORAT DAN PEMBEBANAN PENGISI TERHADAP SIFAT PRA-BIODEGRADASI KOMPOSIT POLIETILENA BERKETUMPATAN TINGGI TERKITAR SEMULA (rHDPE) TERISI SERBUK KAYU MERANTI

ABSTRAK

Tujuan kajian ini adalah untuk mengkaji kesan pembebanan serbuk kayu (WF) dan kesan anti kulat zink borat (ZB) terhadap sifat komposit kayu plastik (WPCs) melalui penanaman dalam tanah dan ujian blok agar. WPCs terdiri daripada polietilena berketumpatan tinggi terkitar semula (rHDPE) dan serbuk kayu (WF) meranti diproses menggunakan penyemprit skru kembar yang kemudiannya diacuan menggunakan pengacuanan suntikan dan pengacuanan mampatan untuk membentuk sampel lenturan. Bagi mengkaji kesan ZB, kandungan WF untuk ujian blok agar ditetapkan pada 50 wt.% dengan kandungan antikulat ZB dari 0.5, 1.0 dan 1.5 wt.%. Sampel komposit berbentuk lenturan didedahkan kepada kulat perang, Gloeophyllum Trabeum (GT) atau kulat putih, Corilous Versicolor (CV) sehingga 12 minggu. Komposit dengan formulasi yang sama digunakan untuk penanaman dalam tanah sehingga 48 minggu di Universiti Sains Malaysia, Nibong Tebal. Kehilangan berat, kandungan lembapan, morfologi permukaan dan sifat lenturan dikaji. Ujian blok agar dan penanaman dalam tanah menunjukkan ZB mencegah biodegradasi pada pembebanan ZB serendah 1.5 wt. %. Morfologi permukaan membuktikan tiada atau kurang jaringan kulat pada permukaan komposit yang mengandungi ZB. Penambahan ZB ke dalam komposit juga mengurangkan kehilangan sifat lenturan selepas pendedahan. Kesan pembebanan serbuk kayu melalui kaedah pra-penyesuain terubahsuai dan penanaman dalam tanah telah dikaji selama 24 bulan. Prapenyesuaian terubahsuai adalah penanaman dalam tanah melalui rendaman air (WS) dan/atau lelasan (S) yang dilakukan di dalam makmal. Penanaman dalam tanah di lapangan dan di dalam makmal menunjukkan pereputan meningkat dengan peningkatan pembebanan WF. WS mempengaruhi serangan terhadap komposit. WPCs melalui WS memberi kehilangan berat dan kandungan lembapan yang lebih tinggi daripada S. Penafsiran dari kedua-dua analisis ZB dan pembebanan WF mendapati penyerapan air menyumbang sedikit kepada penurunan kekuatan dan mempengaruhi peningkatan kehilangan berat.

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ABSTRACT

The aim of this study was to investigate the effect of wood loading and effect of Zinc Borate (ZB) on strength on wood plastics composite (WPCs) properties via soil burial and agar block test. WPCs consisting recycled high density polyethylene (rHDPE), ZB and meranti wood flour (WF) were compounded by twin screw extruder then molded using injection molding and compression molding into flexural shape samples. In order to study the effect of ZB, the composite samples were exposed to brown rot, Gloeophyllum Trabeum (GT) or white-rot fungus, Corilous Versicolor (CV) up to 12 weeks. The composite also used for field soil burial up to 48 weeks at Universiti Sains Malaysia, Nibong Tebal. Weight loss, moisture content, surface morphology and flexural properties were measured. Agar block test and field soil burial demonstrated that ZB prevented biodegradation at ZB loading as low as 1.5 wt.%. The surface morphology revealed the evidence of none or lack of mycelium on the surface of composite containing ZB. Adding ZB to the composite also decreased flexural properties loss after exposure. The effect of WF loading through the method of modified preconditioning and soil burial has studied up to24 weeks. Modified preconditioning is soil burial through water soaking (WS) and/or sanding(S) which was done in laboratory condition. Field and laboratory soil burial demonstrated that decay susceptibility increased with WF loading. WS affected the susceptibility of the composite. WPCs via WS showed higher weight loss and moisture content than S. Interpretation of both ZB and WF loading analysis indicate that moisture absorption contribute little bit to strength loss and influence the increasing of weight loss.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Over the past few years, research and development of wood plastics composites (WPCs) has been gaining more interest among the researchers. Especially in the last decade, the perspective of some plastics industries has changed dramatically. Interest has been fueled by the success of several WPC products, greater awareness and understanding of wood, developments from equipment manufacturers and additive suppliers, and opportunities to enter new markets, particularly in the large-volume building applications sector (Joseph et al., 2006; Winandy et al., 2004; Clemons 2002a).

The term WPCs refers to wood, as fillers in plastic composites. It can be wood flour or sawdust, or agricultural plant residues, typically cut, milled, or ground, or other types of natural fiber, such as kenaf, jute, rice husk, and wheat straw (Morreale et al., 2008; Klyosov, 2007). Thermoplastics that are usually used in WPCs include commodity plastics such as polyolefins (polyethylene(PE)), polypropylene(PP)), polyvinyl chloride(PVC) and biodegradable plastics like **Poly (butylene succinate**) (PBS) and Poly (lactic acid)(PLA) (Morreale et al., 2008; Klyosov, 2007).

During the last few decades, ecological concerns and increasing quantities of plastics waste have resulted in the use of recycled plastics and wood waste (both from post consumer and post industrial material) in WPCs (Adhikary et al., 2008; Winandy et al., 2004). Both recycled plastics and waste wood are cheaper than the virgin. Thus, increased use of recycled plastics and waste wood offers the prospect of lessening waste disposals and reducing the product cost (Cui et al., 2008; Adhikary et al., 2008).

WPCs are used in outdoor applications such as building products (decking, although fencing, industrial flooring, window framing), furniture and automotive products (Ashori, 2008; Clemons, 2002a). WPCs are promoted for outdoor applications because of low maintenance, wood look and exhibit better durability than the solid wood (Wechsler and Hiziroglu, 2007; Clemons, 2002b; Wolcott and Englund, 1999). However, the use of WPCs for outdoor applications has resulted in concern about the durability of these products when exposed to outdoor environments like moisture (from rain and atmosphere) and fungal attack. These environments may degrade WPCs resulting in color changes and/or some decrease in mechanical properties (Schirp et al., 2008; Pilarski and Matuana, 2005; Morrell, 2002). Three approaches have been suggested to improve the durability of WPCs for outdoor applications: (1) surface modification of the wood component (Pothan et al., 2008; Schirp et al., 2008); (2) the use of appropriate coupling agents (Godavarti, 2005, Rowell, 2005); and (3) the use of additives such as fungicides, lubricants and UV-stabilizers (Klyosov, 2007; Caulfield et al., 2005). Zinc borates (ZB) have been introduced as wood preservatives. ZB has low water solubility and is resistant to leaching. Accelerated decay tests indicate that ZB is an effective fungicide and it takes at least 20 years or longer to leach out from WPCs (Tsunoda et al., 2002).

1.2 **Problem Statement**

Exposure to harsh environmental conditions can result in decay on WPCs. Basidiomycete and soft-rot fungal was found to grow on WPC boardwalk in Everglades National Park in Florida (Ibach and Clemons, 2004). WPCs with more than 60 percent wood fiber seem to experience greater fungal decay loss in flexural strength than those using less than 60 wt.% wood fiber (Verhey et al., 2001). If the plastic and wood are mixed in a suitable ratio (low wood content) so that continuous plastic phase exist in the composites, the wood particles should be encapsulated and protected from the effect of moisture and fungal attack (Verhey et al., 2001, Verhey and Laks, 2002). In general, the higher the wood flour content, the greater the potential for biological decay to occur. This is because of the insufficiency of polymer matrix to totally encapsulate the entire wood component. The expose wood particle will facilitate moisture absorption and fungal attack to the composite. To overcome this issue fungicide as Zinc Borate will be used to prevent fungal attack in the composite.

In this research, WPCs were produced from recycled HDPE and meranti wood flour (50 wt. %). The effects of fungicides and filler loading on the resistance to biodegradation of the composites were investigated via soil burial, soil block test and modified preconditioned sample prior to laboratory soil burial. ZB was used as fungicide for the composites. Decay resistances of the composites were evaluated by flexural testing and changes in weight and appearance.

1.3 **Research Objectives**

The present study aims to study the decay resistance of WPCs via soil burial and agar block test. The main objectives of this study are:

1. To study the effect of agar block test, soil burial test and modified preconditioned sample on the composite properties.
2. To study the effects of zinc borate and filler loading on the properties of the WPCs.

CHAPTER 2

LITERATURE REVIEW

2.1 **Composites**

Composites are used in many applications such as in cars, furniture, tennis racket, fishing rods and many more. Composites are any multiphase materials that exhibit a significant proportion of the properties of both constituent phases so that a better combination of properties is achieved (Biron, 2007; Callister, 2003). Most composites have been created to improve combination of mechanical properties such as toughness, stiffness, impact strength, and high temperature strength. The properties of composites are a function of the properties of the constituent phases, their relative amount, and the geometry of the dispersed phase (Callister, 2003).The dispersed phase geometry in this context means the shape of the particles and the particle size, distribution, and orientation (Callister, 2003).The matrix phase of a composite may be a metal, polymer or ceramic (Matthews and Rawlings, 1999). Polymer matrix composite can be thermoplastic or thermoset as a matrix phase.

2.1.1 **Thermoplastic**

Thermoplastics have the simplest molecular structure, with chemically independent macromolecules and by heating, they are softened or melted, then shaped, formed, welded, and solidified when cooled (Biron, 2007). Multiple cycles of heating and cooling can be repeated without severe damage, allowing reprocessing and recycling (Biron, 2007).Thermoplastic materials are, in general are ductile and tougher than thermoset materials. The materials are used in nonstructural applications (Bledzki and Gassan, 1999). Most thermoplastics are high-molecular-weight polymers whose chains

associate through weak Van der Waals forces (polyethylene); stronger dipole-dipole interactions and hydrogen bonding (nylon); or even stacking of aromatic rings (polystyrene) (Pothan, 2008). Many thermoplastics materials are addition polymers; e.g., vinyl chain-growth polymers such as polyethylene and polypropylene (Peacock, 2000). Thermoplastic polymers consist of long polymer molecules that are not linked to each other. i.e., have no cross-links (Pothan, 2008). They are often supplied as granules and heated to permit fabrication by methods such as molding or extrusion.

Types of thermoplastics include commodity plastics, engineering plastics, and specialty plastics. Commodity plastics are used in high volume in the market examples are polyethylene (PE) (bottles, packaging films toys), polypropylene (PP) (carpets, ropes, strapping tapes), polyvinyl chloride (pipe, tote bins, house siding) and polystyrene (fast food containers, wall insulations, disposable drinking cups). Engineering thermoplastics were originally identified by their ability to replace metallic parts in applications such as automobiles, appliances, and house wares. There are polyamides or nylon (hosiery, carpets, molded industrial parts), thermoplastic polyesters (textile applications, films) and polycarbonate (bulletproof windows, compact discs, microwaves containers) (Strong, 2000). Specialty plastics are usually costly, because the processes for making these plastics are expensive (Dyson, 1998).

Specialty plastics offer a unique combination of properties for a particular application. Examples are polyelectrolytes (as coagulants and flocculants for colloidal dispersions e.g. in water treatment and for complex formation), polymer colloids (pharmaceutical and medical applications; tablets, paper making and printing, coating industry) and biomedical polymers (polytethylene; used for articulation surfaces in

joints, in implants and in repair of chest wall and diaphragm) (Galaev and Mattiasson, 2007, Dyson, 1998).

Thermoplastic polyolefins (PP and PE) are the most widely used commodity thermoplastics. Polyolefin are synthetic polymer of olefinic monomers (Pothan, 2008). They are the largest family polymer by volume production and consumption. Polyolefin have a wide range of properties and low costs make them a great success due to many application opportunities.

The characteristics of polyolefin composites are determined by the properties of their components, compositions, structure, and interactions. Polyolefin composites maybe prepared by processes that involve mixing and/or melting the components in a batch or in continuous mixers (single and twin screw extruder), followed by fabrication (molding, thermoforming) into the desired shape (Pothan, 2008).

PE comes in various forms differing in chain structures, crystallinity, and density levels. PE is a semicrystalline polymer. It means that at ambient temperature the polymer consists of two rather distinct fractions, or phase – crystalline and amorphous. The amorphous part of polyethylene, which is sort of rubbery at ambient temperatures, becomes a glass-like at a certain temperature, so called glass transition point (Klyosov, 2007). PE is rather soft, making PE based composite easier to nail, screw, cut, and saw. PE as well as PP, shows near zero moisture absorption (typically below 0.02 % after 24 hour underwater immersion) and very high resistance to chemicals, including strong acids, such as sulfuric and hydrochloric (Klyosov, 2007). PE shows a relatively high resistance to oxidation compared to other polyolefins, hence, requires lesser antioxidants or colorants for processing and for the outdoor applications (Biron, 2007; Peacock, 2000).

The main type PE are high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultralow density polyethylene (ULDPE), and ultrahigh molecular weight polyethylene (UHMWPE). PE resins, that are employed in wood plastics composite (WPCs) include, HDPE (Yuan et al., 2008; Karimi et al., 2007; Stark et al., 2004; Raj et al., 1991), and LDPE (Rodrigo and Greus, 2001).

The general structure of HDPE is shown in Figure 2.1. HDPE produced by Ziegler Natta polymerization leads to linear unbranched PE, permits the development of high degree of crystallinity PE, which is denser, tougher, chemical inertness, highest stiffness and lowest permeability among of all types of PE (Peacock, 2000). HDPE also has better thermal and creep behavior than LDPE, lower coefficient of friction and higher pressure strength, allowing antifriction application with higher PV (pressure velocity) factor, and more transparent (Biron, 2007). From all the good properties combination makes HDPE suitable used for blow molding (household chemical bottles, liquid food bottles, drugs, cosmetics, toiletries), injection molding (food and beverages containers, house wares, crates and totes), films for food packaging and retail bags, sheets, pipes and conduits and many more (Biron, 2007; Peacock, 2000).

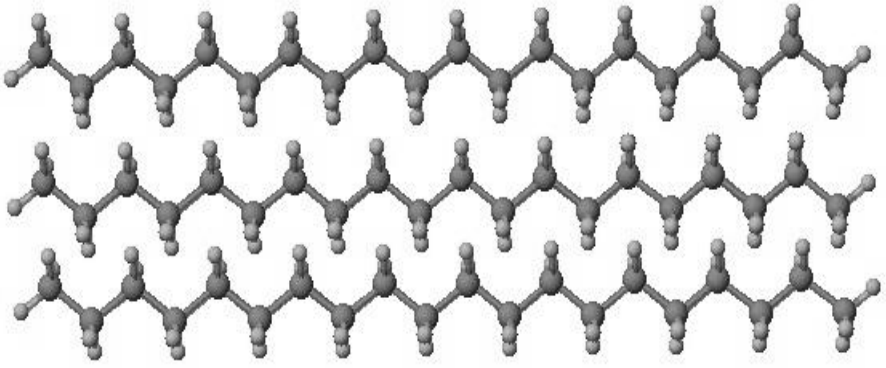

Figure 2.1: A structure of high-density polyethylene (HDPE) (Peacock, 2000)

The worldwide production and consumption of plastics result in a significant contribution to municipal solid waste (MSW). Attempts have been made to recycle the consumer plastics and paper in order to reduce the environmental impact and the consumption of the virgin plastics. There are many reports on the use of recycled HDPE obtained from the post consumer bottles and containers (milk and drinking bottles) (Cui et al., 2007; Adhikary et al., 2007; Kamden et al., 2004). The high volume of plastic waste on the municipal solid waste makes recycled plastics cheaper than competitive material and easy to get. By using recycled plastics rather than virgin, thereby helping the burden of waste disposal in the landfills and can help all humankind to have greener world (Cui et al., 2007). Winnady et al. (2004) reported that recycled sources of both wood and plastics are commonly used in WPCs (Table 2.1).

2.1.2 **Lignocellulosic Filler**

According to Rowell et al. (2005), any substances that contain both cellulose and lignin in the cell walls of woody plants are a lignocellulosic. Lignocellulosic include wood; agricultural crops, like hemp and kenaf; agricultural residues, like rice hull and bagasse; grasses, seed and other plant materials (Rowell et al., 2005).

Agricultural crops vary in terms of chemical composition, structure, and dimensions, and originate from different parts of the plant. Based on the part of the plant from which they are obtained, plant fiber are classified as fruit fiber (from seed-hairs and flosses), bast fiber (fiber bundle extract from the inner bark or stem, through retting process), and leaf fibers (fibers are embedded in a pulpy tissue which needs to be removed by mechanical scraping, called ,decortications (Marsh, 2008). Figure 2.2 shows a classification of natural fiber.

Table 2.1: Listing of common sources for the plastic and wood fiber used in some commercial wood plastic composite products commercially marketed in the United States (Winandy et al., 2004)

Company name	Plastic Resource	Wood Source	Plastic type	Plastic content (%)	Wood content (%)
Trex	Recycled	Pallets and furniture waste	PE	50	50
Crane Plastics	Virgin	Recycled oak wood flour	HDPE	50	50
Fiber composites	Recycled and virgin	Oak and pine from millwork	HDPE, LDPE, PVC	50	50
AERT	Recycled and virgin	Reclaimed cedar wood chips, oak millwork	PE		
USPL	Recycled	Wood and natural fiber	HDPE	65	35
Anderson	Recycled and virgin	Pine scrap	PVC	50	50
Nexwood	Recycled	Rice hull flour	HDPE	40	60
LP specialty product	Recycled	All sawmill waste	PE	50	50
Mikron	Virgin	Hardwood and softwood flour	HDPE, LDPE		
Certain Teed		Recycled fiber	PVC	Max. 65	Max. 45
Kadant Composites	Recycled	Recycled paper fiber	HDPE	40	60
Dura products	Recycled	Pallets and post industrial oak fiber	HDPE		
Correct building products	Virgin	Oak and pine wood fiber	PP	40	60

Wood is and always has been a major material for construction, tools, paper-making, fuel, weapons, and, more recently, as a source for cellulose. The used of wood flour (Baileys et al., 2003) as a filler is a choice offering an economical solution for the increasing costs of wooden products and construction materials. The product develop has the aesthetical appearance wood and the processing capability of thermoplastics.

Although opportunity exists for other sources of wood to be used as filler materials for thermoplastics, wood flour being commercially available resources derived from post industrial scrap, is the most commonly used wood derived fillers today (Kuo et al., 2009; Cui et al., 2008; Sun et al., 2002).

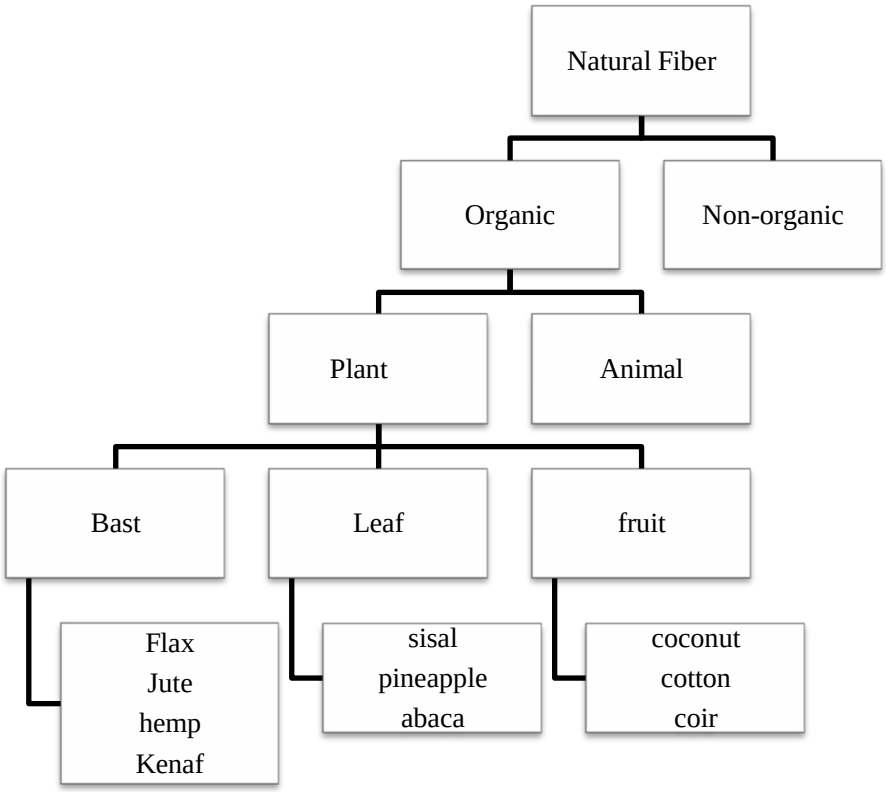

Figure 2.2: A classification of natural fiber (Godavarti, 2005)

2.1.2.1 **Meranti wood flour**

Meranti is the commercial name applied to four groups of species of Shorea, the family Dipterocarpaceae from Southeast Asia, most commonly Malaysia, Indonesia and the Philippines. The four group of meranti are separated on the basis of heartwood color and weight (Table 2.2). About 70 species of shores belong to the light and dark meranti

group, 22 species to the white meranti group, and 33 species to the yellow meranti group.

All the meranti groups are machined easily except white meranti, which dulls cutters as a result of high silica content in the wood. The light red and white meranti dry easily without degrade, but dark red and yellow meranti dry more slowly with tendency to wrap. The strength and shrinkage properties of the meranti groups compare favorably with that of northern red oak. The light red, white, and yellow meranti are not durable in exposed conditions or in ground contact, whereas dark red meranti is moderately durable. Generally, heartwood is extremely resistant to moderately resistant to preservative treatments. Species of meranti constitute a large percentage of the total hardwood plywood imported into the United States. Other uses include joinery, furniture and cabinetwork, molding and millwork, flooring and general construction. Some dark red meranti is used for decking (Miller, 2007).

2.1.2.2 **Chemical composition**

Wood is best define as a three-dimensional biopolymer composite composed of an interconnected network of cellulose, hemicelluloses, and lignin with minor amounts of extractives and inorganic (Rowell et al., 2005). Wood flour is finely divided ground wood having a flour-like appearance. Wood flour that is typically used in WPCs has mesh size about 50-150 μm, 100-200 μm, 200-450 μm, and 250-700 μm. Particle size will affect the processing and properties of composites (Klyosov, 2007).

Table 2.2: Woods belonging to Shorea and Parashorea genera (Miller, 2007)

Name	Color	Density
Dark red meranti (also called tanguile and dark red seraya	Dark brown; medium to deep red, sometimes with a purplish tinge	640+ kg/m^3
Light red meranti (also called red seraya)	Variable-from almost white to pale pink, dark red, pale brown, or deep brown	400 to 640 kg/m^3 Averaging 512 kg/m^3
White red meranti (also called melapi)	Whitish when freshly cut, becoming light yellow-brown on exposure to air	480 to 870 kg/m^3
Yellow meranti (also called yellow seraya)	Light yellow or yellow-brown, sometimes with a greenish tinge; darkens on exposure to air	480 to 640 kg/m^3

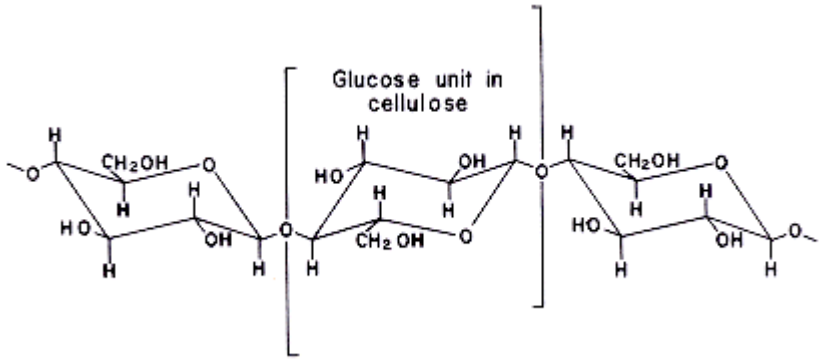

Figure 2.3: A part of cellulose structure (Pothan, 2008)

Cellulose is the most abundant organic chemical on the face of the earth. It is a linear condensation polymer consisting of D- anhydroglucopyranose units, joined together by β-1-4-glycosidic bonds (Gassan and Bledzki, 1999). The chemical character

of the cellulose molecule is determined by the sensitivity of the glucosidic linkages, between the glucose repeating units, to hydrolytic attack, and by the presence of three reactive hydroxyl groups-one primary and two secondary, in each of the glucose base units (Figure 2.3) (Pothan, 2008). The number of glucose units in a cellulose molecule is referred to as the degree of polymerization (Matuana and Kamdem, 2002). Goring and Timell (1962 cited in Rowel, 2005) determined that wood cellulose has an average DP of 9000-10000 and possibly as high as 15000.

There are several types of cellulose in wood; 1) crystalline and noncrystalline and, 2) accessible and nonaccessible (Rowel, 2005). Accessible and nonaccessible refer to the availability of the cellulose to such as water and, microorganism. Most of the noncrystalline cellulose is accessible but part of the noncrystalline cellulose is so covered with both hemicelluloses and lignin that it becomes nonaccessible (Rowel, 2005). Concepts of accessible and nonaccesible cellulose are very important in moisture sorption, pulping, chemical modification, extractions, and interactions with microorganism (Rowel, 2005).

Hemicelluloses differ from cellulose, in that they contain several sugar units such as galactoglucomanan and arabinoglucuronoxylan, whereas cellulose contains only glucopyranes units. In general, hemicelluloses consist of a collection of polysaccharide polymers with lower DP than cellulose (average DP of 100-200) (Caulfield and Clemons, 2005). Hemicelluloses have short branched chains consisting of five and six carbon ring sugar (Klyosov, 2007).

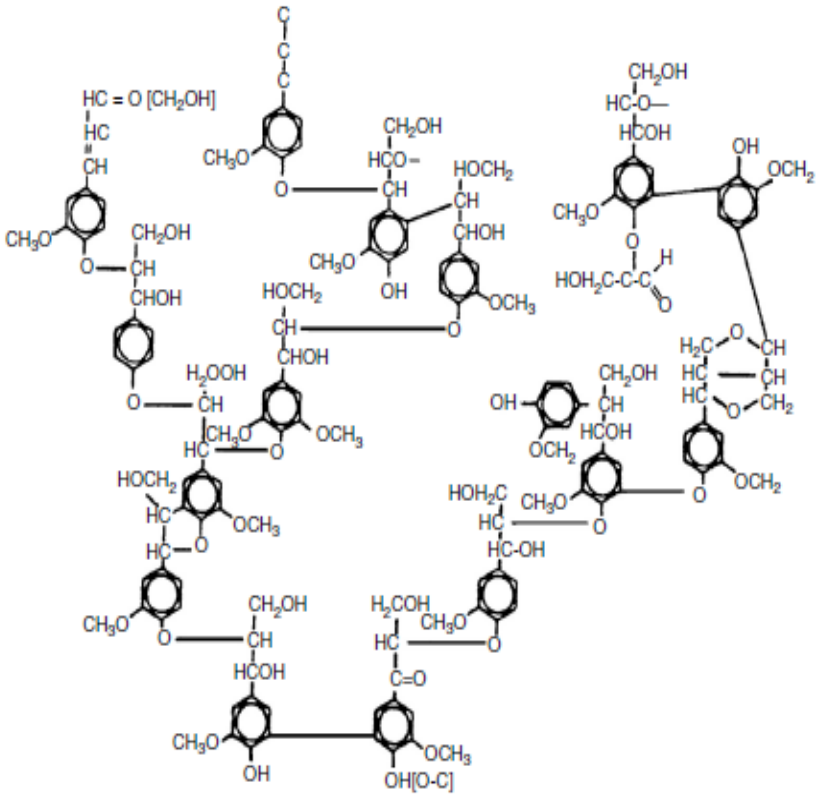

Figure 2.4: Partial structure of lignin (Rowel, 2005)

Lignin is a little understood hydrocarbon polymer with a highly complex structure consisting of aliphatic and aromatic constituents (Figure 2.4) and forms the matrix sheath around the fibers that holds the natural structure (such as trees) together (Kylosov, 2007). Lignin in wood maybe considered to be a random three dimensional network polymer comprised of phenylpropane units linked together in different ways (Glasser and Sarkanen, 1989). The phenylpropane can be substituted at the α, β, or γ positions into various combinations linked together both by ether and carbon to carbon linkages (Rowel, 2005). Through various side linkages these building blocks form large macromolecules.

Lignin results from random free radical polymerization of three closely related phenolic substances (Bodig and Jayne, 1982). Lignin is distributed throughout the secondary cell wall, with the highest concentration in the middle lamella. Because of the difference in the volume of middle lamella to secondary cell wall, about 70% of the lignin is located in the cell wall (Rowell et al., 2005). The mechanical properties of lignin, however, are lower than those of cellulose (Bledzki and Gassan, 1999). Lignin most commonly noted function is the support through strengthening of wood (xylem cells) in trees.

2.1.2.3 **Wood Anatomy**

Wood is porous, fibrous, and anisotropic. Wood is often subdivided into two broad classes, namely softwoods and hardwoods, which are classified by botanical and anatomical features rather than actual wood hardness (Caulfield and Clemons, 2005). Wood is primarily composed of hollow, elongated, spindle-shaped cells (called tracheids or fibers) that are arranged parallel to each other along the trunk of the tree. The lumen (hollow center of the fibers) can be completely or partially filled with deposits, such as resins or gums, or growths from neighboring cells called tyloses. These fibers are firmly cemented together and form the structural component of wood tissue (Caulfield and Clemons, 2005).

Cell wall in wood is a non-homogenus membrane (Figure 2.5). Cell walls contain several layers which include the middle lamella (ML), which is free of cellulose, primary wall (P) and outer layer of the secondary wall (S1), middle layer of secondary wall (S2) and innermost layer of the secondary wall (S3) (Wiedenhoeft and Miller, 2005). The so-called primary wall (the first layer deposited during cell growth encircling

a secondary layer wall) and the secondary wall (S), which again is made up of three layers (S1, S2 and S3) (Wiedenhoeft, and Miller, 2005).

Cellulose attains its highest concentration in the S2 layer (about 50%) and lignin is most concentrated in the middle lamella (about 90%) which, in principle, is free of cellulose. The S2 layer is usually by far the thickest layer and dominates the properties of the wood. The S2 layer consists of a series of helically wound cellular microfibrils form long chain cellulose molecules. Such microfibrills have typically a diameter of about 10-30 nm and are made up of 30-100 cellulose molecules in extended chain conformation and provide mechanical strength to the wood (Rowel, 2005; Jayaraman, 2003).

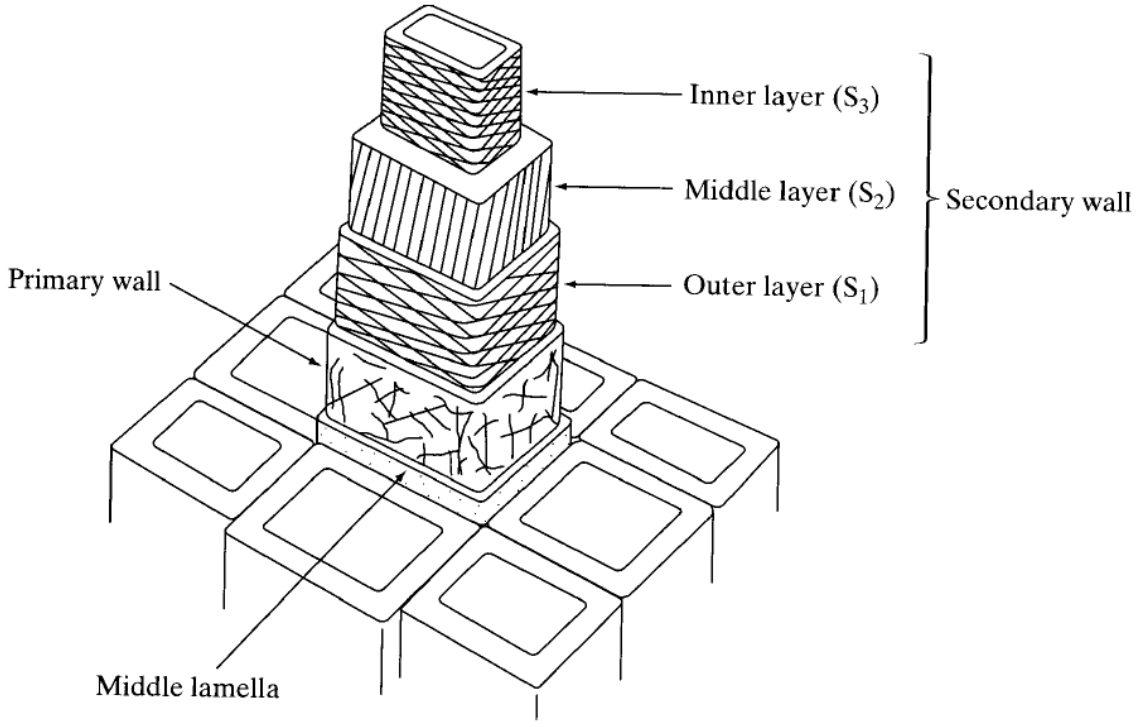

Figure 2.5: A schematic diagram to illustrate the three dimensional of cell walls (Wiedenhoeft and Miller, 2005)

2.1.2.4 **Advantages and disadvantages**

Polymer composites featuring both stiffness and strength have been of great commercial interest for a century now. Although inorganic fillers such as calcium carbonate, mica, fiberglass, talc and clay have been widely used, composite containing lignocellulosics fillers, derived from renewable and recyclable sources have aroused broad interest (Pothan., 2008). Lignocellulosic fillers offer many advantages that make them more attractive than the traditional materials as fillers and reinforcement for thermoplastics. Table 2.3 shows a comparison between natural filler and glass fiber.

Table 2.3: A comparison between natural filler and glass fiber (Kaczmar and Pach., 2007)

	Natural filler	Glass fiber
Density	Low	Twice that natural fiber
Cost	Low	Low, but higher than natural fiber
Renewable	Yes	No
Recyclable	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO_2 neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Non biodegradable

Lignocellulosic fillers relatively lower density, lower cost, and less processing equipment abrasion than traditionally inorganic filler/fiber (Albano and Perera, 2008; Marsh, 2008;). Lignocellulosic fillers also can be recycled and are carbon neutral since

carbon dioxide (CO_2) emitted during production is reabsorbed by new plant growth (Marsh, 2008). They pose no risk to human health when fiber/flour particles are inhaled, and at the end of life they are biodegradable (Marsh, 2008). They also easy to handle and present no health problem like glass fiber that can cause skin irritations during processing (Ashori, 2007; Bledzki et al., 2005; Oksman and Clemons, 1998). Because of non toxic nature of lignocellulosic filler, the waste management is easy to handle than glass fiber (Ashori, 2007; Oksman and Berglund, 2002). Plastic machinery is not damaged by lignocellulosic fibers because of their non abrasive nature. This permits high levels of filling in composite with high stiffness without usual machine wear problem associated with glass fiber. Thus also makes recycling, production, and technical process easier and competitive (Ashori, 2007; Lavendal, 1996).

Albeit all the advantages as mention above, there are certain drawbacks, such as tendency to form aggregates during processing, low thermal stability, low resistance to moisture and seasonal quality variations (even between individual plans in the same cultivation). These disadvantages greatly limit the potential of using lignocellulosic fiber in plastic industries (Kim et al., 2006). Moisture absorption of lignocellulosic fillers can result in swelling and presence of voids at the interface (porous product) of the fillers resulting in dimensional instability and poor mechanical properties (Bledzki and Gassan, 1999; Simonsen and Jacobsen, 1998).

Lignocellulosic is not compatible with polymer matrices such as PE and PP. This result in non-uniform dispersion of fillers within the matrix and poor mechanical properties (Cui et al., 2008; Tserki et al., 2006; Simonsen and Jacobsen, 1998). Most polymers, especially thermoplastics, are nonpolar (hydrophobic) substances, which are not compatible with polar (hydrophilic) wood fillers, therefore, poor adhesion between

matrix and fillers can result in composite leading to poor mechanical properties (Kim et al., 2006; Lai et al., 2003).

All of these factors limit the service life of wood plastic composites particularly in outdoor applications. Many studies have been carried out to improve the use of lignocellulosic filler as reinforcement in thermoplastics. The reinforcement of composites with lignocellulosic fillers is dependent on cellulose content, moisture content, and fillers – matrix interfacial adhesion (Bledzki et al., 2005).

Several techniques have been applied to modify the surface of lignocellulosic fillers in order to reduce the hydrophilicity and to minimize the interfacial energy with nonpolar polyolefinic matrices (Pothan, 2008). Bledzki et al. (2005) have given detail review on the various strategies in modifying lignocellulosic fillers for use as reinforcing element in composite materials. They have classified the major approaches of fiber treatment include, (i) physical treatments such as solvent extraction, (Clausen et al., 2007) physicochemical treatments, like the use of corona and plasma discharges or laser,X-ray, and ultraviolet (UV) bombardment(Clausen et al., 2007) and chemical modifications, by direct condensation of the coupling agents onto the cellulose surface and by various grafting strategies including polycondensation and free radical or ionic polymerization (Pothan, 2008; Bledzki et al., 2005). Chemical modification of wood involves various chemical treatments with the aim to reduce the number of –OH groups of the fiber or to introduce crosslinking by physical and chemical bonds between the filler and the polymer matrix. The chemical coupling reactions used in modifying lignocellulosic filler surfaces can mainly classified as i) esterification, (Clausen et al., 2007) (ii)etherification (Clausen et al.2007) (iii) urethane formation and (iv) siloxane formation (Pothan, 2008).

Lignocellulosic fillers are a biodegradable material that can be degraded under proper conditions. Wood degradation can be classified as damage caused by biotic (living) and abiotic (non-living) agents (Morell, 2005). Abiotic agents include weathering, mechanical wear, chemicals, salts and heat. Basically a conditions essential for fungal growth in wood are food, sufficient oxygen, suitable temperature, and adequate moisture (Stark and Gardner, 2008; Morell, 2005). Wood itself provides the necessary food (Glasser et al., 1989), and oxygen is readily available in the environment. Decay will perform at approximately 20% moisture content (Stark and Gardner, 2008; Wang and Morrell, 2005). Below this level degradation due to fungal attack will not occur, and fungi that may have already begun to grow will cease growing (Naghipour, 1996). To prevent degradation occur, it involves removing or limiting one or more of the four basic requirements for biological degradation. All of this can be done via treatment of fiber, adding preservatives, or fiber modifications (Wang and Morrell, 2005).

2.1.2.5 **Biodegradation**

Fungi that attack wood include the decay fungi and stain or mold fungi. Decay fungi have the most deleterious impact on wood in service because the organisms consume the primary wood chemical components. Decay fungi are single-called or multicellular filamentous organisms that use wood as food. Figure 2.6 shows decay cycle of wood. Following infection by air-borne spores or by contact with infected materials, the fungus develops within the wood, forming microscopic, thread-like structures known individually as hypha (plural hyphae) and collectively as mycelium, commons forms of which are shown in Figure 2.6. Under favorable conditions, hyphae

may also develop on the surface of wood, or in checks or other opening within it, as closely woven strands or rootlike masses or feltlike (frequently fan-shaped) mycelia mats, which are usually white or shade or brown and readily visible to the naked eye (Ibach, 2005; Hunt and Garratt, 1967).

These hyphae secrete enzymes that attack the cells and cause wood to deteriorate (Ibach, 2005). After serious decay, a new fruiting body may form and spread to whole wood.

Decay fungi are grouped into three types including white-rot, brown-rot (both basidiomycetes), and soft-rot (ascomycetes) (Wang and Morell, 2005). All of this fungus appears to have enzymatic systems that demethoxylate lignin, produce endocellulases, and with some fungi from each group, use single electron oxidation systems to modify lignin (Eaton and Hale, 1993 cited in Hunt and Garratt, 1967). White – rot fungi decomposed all the structural components (i.e., cellulose, hemicelluloses, and lignin) from wood.

As the wood decays it becomes bleached and white black zone lines. The degraded wood does not crack across the grain until it is severely degraded. It keeps outward dimensions but feels spongy. The strength properties decrease gradually as decay processes, except toughness. White –rot fungi have complex cellulose and also the ability to degrade lignin (Ibach, 2005).White-rot fungi primary attack lignin and leave behind a cellulose-rich residue, while brown-rot primarily attack carbohydrates and leave behind a lignin-rich residue.

The wood becomes brown (thus the name). Because of the attack on the cellulose, the strength properties of brown-rot decayed wood decreased quickly, even in the early stages. When extreme decay is attained, the wood becomes a very dark, charred color. After the cross-grain cracking, the wood shrinks, collapses, and finally crumbles.

Brown-rot fungi first use low molecular weight system to depolymerize cellulose within the cell wall and then use endocellulose to further decompose the wood (Ibach, 2005). Brown-rot fungi attack mainly softwood while white-rot fungi attack primarily hardwoods. However, each fungal type can be found on both softwoods and hardwoods (Ibach, 2005). Soft-rot fungi typically produce chains of cavities with conical ends in the secondary wall of wood (Ibach, 2005).

In the early or incipient stage of wood decay, the hyphe may spread through the wood in all direction from the point of infection, usually passing from cell to cell through bore holes (Figure 2.6), which they form at the point of contact between the hypha and cell wall, or through the natural opening (pits). During this invasion stage, there usually is no apparent change in appearance of the wood, other than a slight discoloration of the infected piece (Klyosov, 2007; Ibach, 2005).

Bore holes and general dissolution of the cell walls become more conspicuous, and the wood undergoes marked changes in color, texture, continuity, strength properties. In the late or advanced stage decay, the wood becomes punchy, soft and spongy, stringy, ring-shaked, pitted or crumbly, depending upon the nature of the attacking fungus and the extent of its affect on the wood (Hunt and Garratt, 1967). Serious strength losses can occur before it is even detected. Toughness, or impact bending, is most sensitive to decay. With incipient decay the wood may become discolored on unseasoned wood, but it is harder to detect on dry wood (Ibach, 2005). The advanced stages of wood decay are easier to detect. Decayed wet wood will break across the grain, whereas sound wood will splinter.

Decay fungi need food (hemicelluloses, cellulose, and lignin), oxygen (air), the right temperature (10 to 35 ^{o}C; optimum 24 to 32 ^{o}C), and moisture (above fiber

saturation point; about 20% moisture content) to grow. Free water must be present (from rain, condensation, or wet ground contact) for the fiber saturation point to be reached and decay to occur. Air-dried wood will usually have no more than 20% moisture content, so decay will not occur (Ibach, 2005). But there are a few fungi, water conducting fungi that transport water to dry wood and cause decay to dry-rot. When free water is added to wood to attain 25 to 35 % moisture content or higher, decay will occur. Yet wood can be too wet or too dry for decay. If wood is soaked in water, there is not enough air for the fungi to develop (Ibach, 2005).

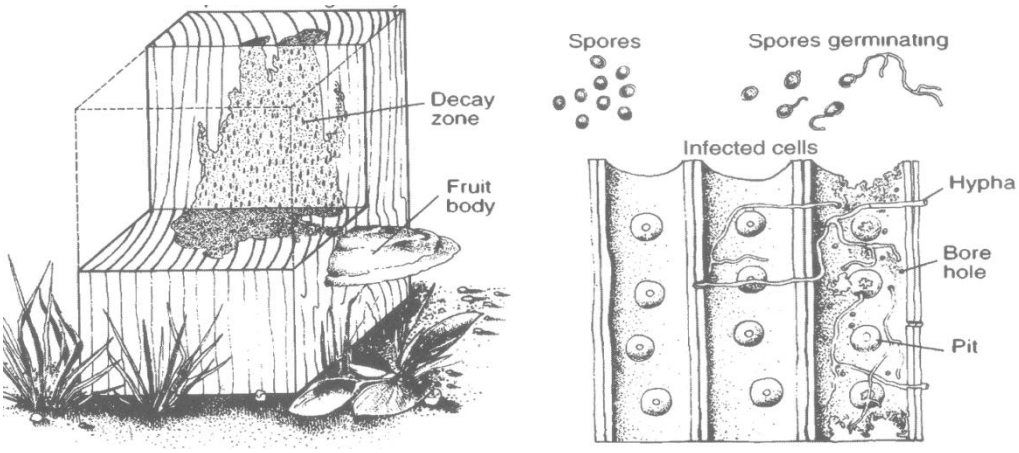

Figure 2.6: The wood decay cycle and section of post showing decay (Ibach, 2005).

2.1.3. **Additives**

To meet the consumer needs and to enhance the properties of composites, additives can be added depending on the applications. Additive is used to ensure long term durability of composite products.

There are many additives that can be used in composites such as colorants, lubricants, coupling agents, UV stabilizers and fungicides.